

Structural Color Circulation in a Bilayer Photonic Crystal by Increasing the Incident Angle

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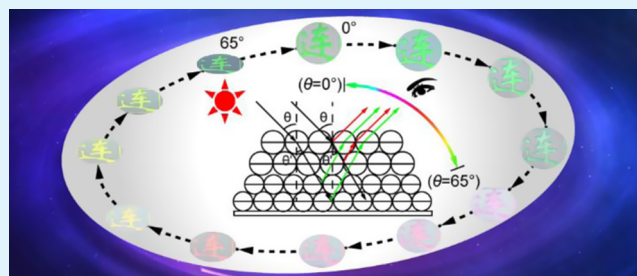
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S Supporting Information

ABSTRACT: Photonic crystals (PCs) have been widely applied in the anticounterfeiting field according to their easily tunable and angle-dependent structural colors. However, most studies are now focused on single-layer PCs assembled from monodisperse colloidal spheres, which have only one bandgap. Here, we prepared bilayer photonic crystal films by choosing 250 and 330 nm silica spheres as the bottom and top layer, respectively. The effect of the incident angle on the bandgap of PCs was investigated and the results showed that the bandgap of the bilayer PCs was incident angle dependent—the structure exhibited two strong bandgaps within small incident angles, while as the incident angle increases, both the bandgaps blue-shifted and more importantly, the bandgap of the bottom layer disappeared with a further increase in the incident angle. Furthermore, with the delicate design of the thickness of the top layer, this bilayer structure selectively displayed the structural colors of the bottom layer, overlap colors of both the top and the bottom layer, and the color of only the top layer, respectively. By changing the incident angle, the color circulation from green to magenta, orange, yellow, and green again was realized. The realization of the controllable color tunability further motivated us towards the patterning of the bilayer PCs, which showed promising potential in the anticounterfeiting field.

KEYWORDS: bilayer PCs, color circulation, thickness, bandgap, structural color mixing



1. INTRODUCTION

Photonic crystals (PCs) are artificial periodic structures with spatially periodic arrangement of the refractive index, which results in the existence of photonic bandgap in the structure.^{1–4} If the photonic bandgap locates in the visible region, the PCs will show brilliant colors, which are called structural colors.^{5,6} Structural colors originating from the photonic bandgap have several characteristics such as angle dependence, crystal lattice dependence, antiphotobleaching, and metal luster, which are greatly different from chemical colors originating from dye molecules or pigments.^{7,8} Due to their unique optical properties,^{4,9–11} many efforts have been made for the application of structural colors in the fields of anticounterfeiting,^{12–16} color displays,^{5,17–19} colorimetric chemical sensors,^{9,20,21} and lasers.^{22–24}

The commonly used artificial three-dimensional PCs are fabricated by self-assembly of monodisperse colloidal spheres²⁵ and therefore possess single bandgaps. Inspired by the strategy to enrich the colors in the dye field through mixing three primary colors, multilayer PCs with double or triple bandgaps have been investigated to realize structural color mixing.^{26–28} These multilayer PCs were well documented to widen the reflection spectra of PCs and to enhance the luminescence of quantum dots, fluorescent dyes, and light-emitting diodes.^{29–31}

It is well known that the structural color of the PCs is angle-dependent, i.e., the structural color will blue-shift with an

increase of the incident angle. The angle-dependence of the structural color makes PCs good candidates for anticounterfeiting applications.^{12–14} Extending the structural color changing tendency upon increasing the incident angle from only blue shift to color circulation within the visible region will enhance its anticounterfeiting capability. At the same time, the scattering effect of PCs enlarges and leads to decreasing reflection intensity at large incident angles.²¹ It can be speculated that in a bilayer PC structure, the structural color of the bottom layer will be weakened more dramatically than that of the top one due to the enlarged scattering effect of both the layers. In this regard, the structural color of the bilayer PCs could be substantially the same as that of the top layer at a certain value of the incident angle. On the other hand, if the bandgap of the top layer is located in the near-infrared (NIR) region, the bilayer PCs will only show the structural color of the bottom layer. In other words, by tuning the incident angle, it is theoretically possible to extend the structural color changing tendency from only blue shift to color circulation within the visible region in the designed bilayers.

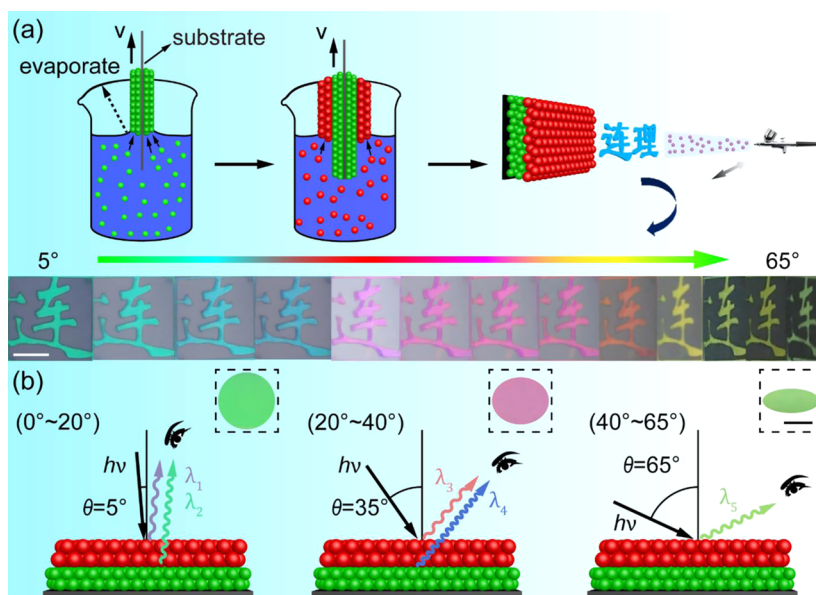
Based on the above analysis, we designed here a bilayer PC structure (Scheme 1a), using 250 and 330 nm silica spheres to

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Scheme 1. (a) Schematic Representation of Bilayer PCs Fabricated by Consecutive Dip-Coating of Monodisperse Silica Spheres with Two Different Sizes and Patterned by Spray-Coating; (b) Generation Mechanism of the Structural Color of the Bilayer PCs under Different Angles; Sizes of the Two Kinds of Silicon Microspheres are 250 and 330 nm, Respectively; (Scale Bar: 5 mm)



build the bottom and top layers by a dip-coating method. The obtained structure displayed the structural color of the bottom layer because the bandgap of the top layer was located in the NIR region during small incident angle changes. With the color of the top layer being blue-shifted to the visible spectrum during incident angles of 20–40°, the bilayer structure demonstrated mixing colors of both the layers. When the incident angle was larger than 45°, only the structural color of the top layer was observed due to the dramatic scattering effect. The generation mechanism of the structural color of the bilayer PCs is shown in Scheme 1b. The structural color of the designed bilayer structure demonstrates a green-magenta-orange-yellow-green color cycle, which is different from the traditional PCs with single bandgaps or multilayer PCs with all bandgaps in the visible region. These results will provide potential applications of this structure in the anticounterfeiting field.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Suspensions. The synthesis procedure of silica microspheres was a modified Stöber process and the particle size of the silica can be tailored by changing the amount of ammonia.³² The prepared colloidal silica spheres were thoroughly washed with ethanol three times by centrifugation and then dried. In this study, to get the desired photonic bandgap of the PCs (the detailed theoretical calculations are given in the Supporting Information), we prepared three kinds of silica microspheres with diameters of 210, 250, and 330 nm, respectively. The scanning electron microscopy (SEM) images of these silica microspheres are shown in Figure S1. Silica microspheres with different sizes were dispersed in *N,N*-dimethylformamide (DMF) to form silica microsphere suspensions with concentrations of 6 wt % (210 and 250 nm) and 8 wt % (330 nm). To disperse the silica microspheres well in the DMF solvent, the suspension should be sonicated for 5–7 h before use.

2.2. Preparation of Bilayer PC Films by Dip-Coating. First of all, the prepared silica microspheres were dispersed in DMF solvent and ultrasonicated for 5–7 h before use. The suspensions of the silica spheres in DMF were transferred into a 10 mL beaker and then the

beaker was placed in a Coater from HeatMent (SYDC-100H DPI, SAN-YAN Instrument Co. Ltd., Shanghai). The temperature during the entire dip-coating process was set to 65 °C. Glass slides were used as substrates, which were first washed with water and then hydrophilized by a plasma cleaner (MTI Corporation PCE-6) before use. The pulling rate was set as 2 μm/s except where specifically noted.³²

2.3. Preparation of Patterned Bilayer Colloidal Crystals. The silica microspheres were dispersed into ethanol at a concentration of 10 wt % as the paint during the spraying process. The average size of the silica particles used is 330 nm. The obtained suspension was put into an airbrush with a nozzle size of 0.2 mm. The airbrush was driven by a gas pump (at 4 bar) and set 8 cm to the substrate. A mask of “连理” was coated on the surface of the as-prepared bilayers. Then, the airbrush was moved back and forth at a speed of ~3 cm/s. Then, with the alcohol solvent volatilizing rapidly, SiO₂ microspheres deposited disorderly on the surface of the pre-prepared bilayer PC without the mask. The entire process of spray-coating was repeated 15 times. Due to the strong scattering effect, the structural color of the part without the mask covered by SiO₂ nanoparticles disappears, thereby realizing the patterning of bilayer PCs.

2.4. Characterization. The reflectance and transmission spectra were recorded using a Hitachi U-4100 spectrophotometer. The schematic of the measurement setup (Figure S2) and the measurement steps have been given in detail in the Supporting Information. The digital photographs of the structural colors of PCs were taken by a cell phone (iPhone) under different incident angles. The specific method (Figure S3) and steps of taking photos have been detailed in the Supporting Information. The morphology of the prepared samples was obtained by using a Nova NanoSEM 450 field emission scanning electron microscope.

3. RESULTS AND DISCUSSION

Crystalline quality is one of the most important factors affecting the bandgap properties of PCs, especially for bilayer PC films. We prepared the bilayer PCs by the consecutive dip-coating method using a drawing machine. In general, the bilayer stacking can be realized by assembling big spheres onto the prepared PC film of smaller ones or in the inverse form. In

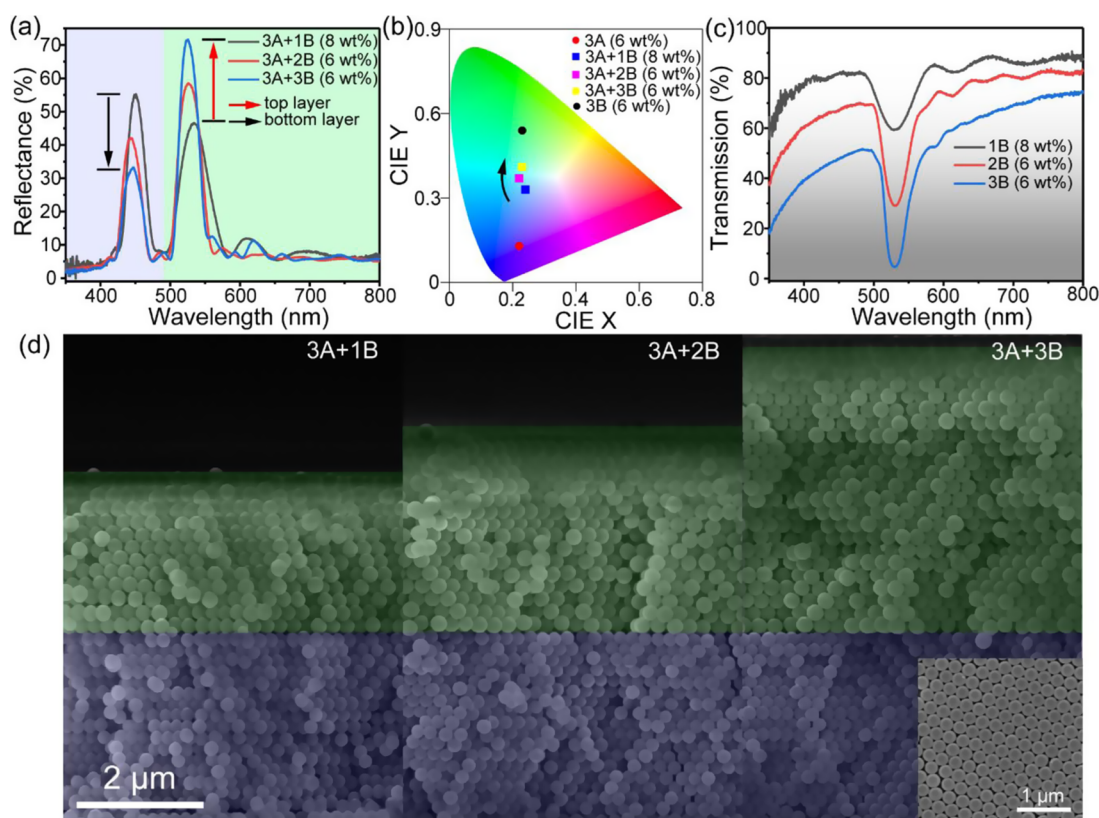


Figure 1. (a) Reflection spectra of the bilayers with different thicknesses of the top layer ($\theta = 10^\circ$). (b) CIE chromaticity diagram obtained by the spectra of (a). (c) Transmission spectra of the PCs with different thicknesses at $\theta = 10^\circ$. (d) Typical cross-sectional SEM images of the bilayer PCs with different thicknesses of the top layer. The inset shows the top view SEM image of the bilayer PCs, and the bilayers with different thicknesses show the same results. (A represents one pulling cycle of 210 nm silica spheres and B represents one pulling cycle of 250 nm silica spheres.)

our work, we choose the former method because larger silica spheres are easier to assemble on a layer of smaller ones than to assemble on a layer of bigger ones because of the rough surface of the layer made from big spheres.²⁶

3.1. Top Layer Thickness and Incident Angle Dependence of the Structural Color in Bilayer PCs. To realize our designed idea that a bilayer PC structure can display the structural color of the bottom layer, the mixing colors of both the top and bottom layers, and the color of only the top layer, respectively, we firstly investigated the top layer thickness and incident angle dependence of the structural color.

In the first step, a 2 μm/s pulling rate and three pulling cycles were applied to fabricate the bottom layer of PCs to get a well-assembled PC film with a relatively strong bandgap.³² For the top layer, its thickness is crucial for the reflectivity of different layers of the bilayer PCs. According to a previous study,³³ increasing the thickness will make the bandgap of PCs narrower and stronger but at the same time, it will decrease the transmittance of the PC layer due to the scattering of the spheres. A suitable thickness of the top PC is particularly important to guarantee the reflected light of the bottom layer to transmit the top layer. Taking silica microspheres with sizes of 210 and 250 nm as examples, we prepared bilayer PCs with the same thickness of the bottom layer (2 μm/s pulling rate, pulling for three cycles) and different thicknesses of the top layer (pulling for one to three cycles) and investigated their optical properties.

As shown in Figure 1d, the dip-coating method enabled silica spheres to self-assemble into a highly ordered arrangement with a face-centered cubic structure. Each layer of PCs

had a highly ordered structure and no obvious disturbed boundary between the layers was observed, which provided strong and narrow reflectance spectra (Figure 1a) and thereby achieved a brilliant structural color. It is obvious that upon increasing the thickness of the top layer, the reflectivity of the top layer was enhanced gradually; in sharp contrast, the reflectivity of the bottom layer was weakened because of the scattering of the lattice planes of the top layer (Figure 1a). Based on these results, the structural color of the bilayer PCs by changing the thickness of the top layer was obtained as displayed in Figure 1b. Considering the reflectivity of the one pulling cycle of the top layer PCs is relatively wide and weak, while three pulling cycles of top layer PCs will weaken the reflectivity of the bottom layer PCs, the two-pulling-cycle process was applied to prepare top layer PCs in the subsequent experiments.

To verify the reflectivity attenuation of the bottom layer that was generated by the scattering effect, the transmittance spectra of the PCs fabricated by different pulling cycles were recorded. As shown in Figure 1c, it is obviously observed that the increased thickness of the PCs indeed enlarges the scattering effect and decreases the transmittance.

According to Bragg's law of diffraction, the bandgaps of PCs are closely related to the angle of the incident light. As reported in ref 21, upon increasing the angle of incident light, not only will the wavelength of the bandgap be blue-shifted but also the reflection intensity will decrease gradually due to the enhanced scattering effect. In a bilayer structure, the bandgap intensity of the bottom layer is supposed to decrease more greatly than single-layer PCs because of the scattering effect of

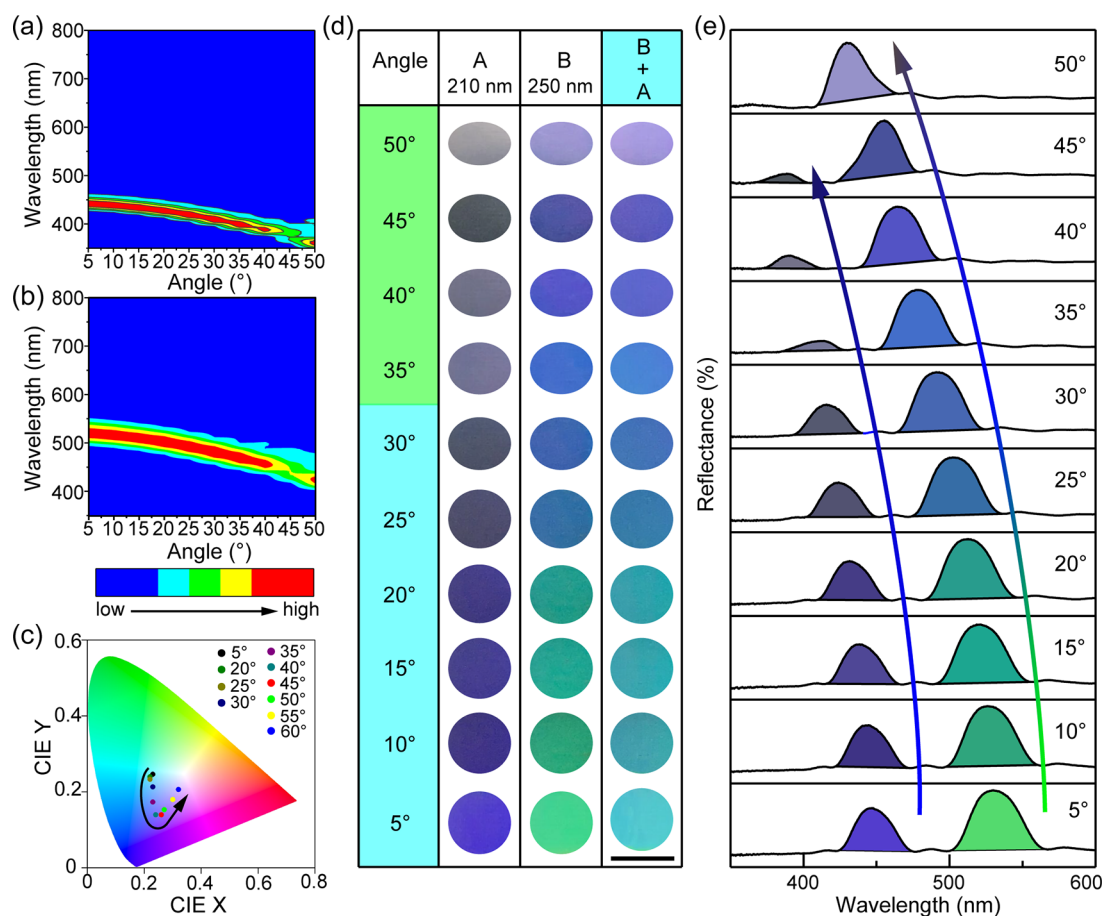


Figure 2. (a, b) Color-filled contour maps of the single-layer PCs assembled from 210 and 250 nm SiO₂ spheres, respectively. (c) Evolution of structural colors of the bilayer structures in the CIE chromaticity diagram. (d) Digital photographs of structural colors of single-layer PCs (210 and 250 nm) and bilayer PCs, taken from different incident angles. (e) Reflectance spectra of bilayer PCs at different incident angles. (The bilayer PCs mentioned here were self-assembled from 210 and 250 nm SiO₂ microspheres. Scale bar (d): 1 cm.)

both the top layer and itself, and at a certain incident angle, the bottom layer bandgap will even possibly disappear. To prove this hypothesis, we recorded the reflectance spectra of the bilayer PCs at different incident angles. Contour maps of single-layer PC films assembled from 210 and 250 nm silica microspheres are shown in Figure 2a,b. In good agreement with the literature, the bandgap of the single layer was blue-shifted and got weakened with the increasing angle of incident light. For the bilayer PC structure, there were two reflection peaks in the reflection spectra when the incident light angle was under 50°, which will realize the superposition bandgaps and resulting overlap of structural colors. The reflectance spectra in Figure 2e indicated that the reflectivity of the bottom layer indeed decreased more greatly than that of the top layer due to the double effects of both the bandgap intensity decrease and the scattering enhancement of the top layer with the increase of the incident angle. At small incident angles (0–30°), two obvious reflection peaks corresponding to each photonic bandgap of the PCs coexisted. As expected, with the incident angle increasing, the reflection peak generated by the bottom PCs was weakened gradually due to the increased scattering of the random light.²¹ When the incident angle is over 35°, the bandgap of the bottom layer became weaker and weaker and its structural color could almost not be observed in this case. Through the transmission spectra (Figure S4), we can find that the transmittance descended with the incident

angle increasing, which also confirmed that the scattering effect hinders the structural color.

To clearly display the structural color variation of the bilayer PCs at different incident angles, we used a digital camera to take photos of the bilayer structures and single-layer PCs at different incident angles (Figure 2d). The colors of the digital photos were basically consistent with the coordinates in the CIE chromaticity diagram (Figure 2c) obtained by the reflectance spectra of Figure 2e. From the digital photos, we can further prove that the bilayer PCs prepared by the dip-coating method achieved the superposition of structural colors produced by mixing two primary colors, at small angles (0–30°). Once the incident angle reaches 35° or larger, the structural color of the bilayer PCs was simply provided by the top layer as the bandgap of the bottom layer nearly disappeared.

All these results indicated that a suitable thickness of the top layer PCs makes it possible to realize a bilayer PC structure, which can display mixing colors of each primary PC structural color and only the structural color of the top PCs through increasing the incident angle.

3.2. Realizing a Whole Spectrum Structural Color Circulation by Designing a Special Bilayer PC. Based on the above results, it can be concluded that the structural color of the bilayer PCs possesses two features. First, two strong bandgaps coexist within smaller incident angles. Second, as the incident angle increases, each bandgap will be blue-shifted and

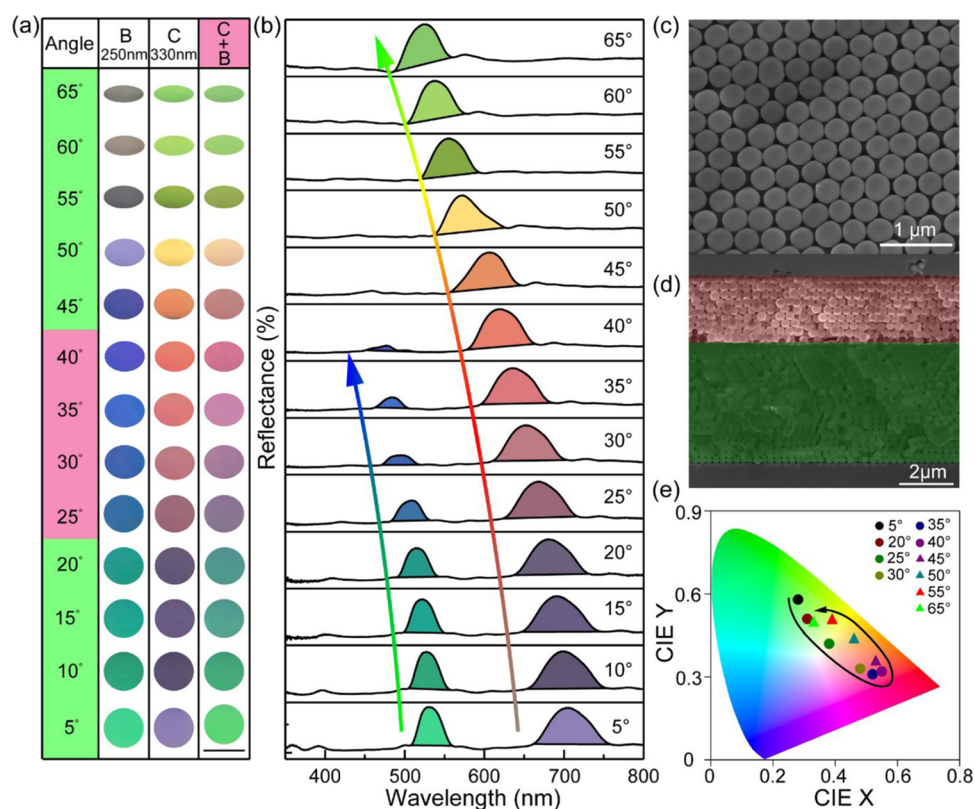


Figure 3. (a) Digital photos of the multilayer PCs at different incident angles. (b) Reflectance spectra of the bilayer PCs assembled from silica microspheres with the particle sizes of 250 and 330 nm. (c, d) Typical SEM images showing the bilayers assembled by 250 and 330 nm SiO₂ microspheres. (e) CIE chromaticity diagram obtained by the spectra of (b). (Scale bar (a): 1 cm.)

more importantly, the bandgap of the bottom layer will be attenuated greater than that of the top one, resulting in the whole structural color of the bilayer structure being dominated by the color of the top layer. That means at all incident angles, the structural color of the bilayer PCs may be the mixing colors of two PCs or the single color of the top layer. Here, to extend the color tunability of the bilayer structure and enhance its anticounterfeiting capability, we designed a special bilayer PC structure. In this structure, the bandgap of the top layer is in the NIR region at small incident angles, and the structural color of the bilayer PCs is only provided by the bottom layer in this case.

According to these aspects, we built bilayer PCs using silica microspheres with diameters of 250 and 330 nm as building blocks, respectively. According to Bragg's law, the bandgap of the PC prepared by 250 nm silica spheres is located in the visible region (green to blue) at all incident angles. However, the bandgap of the PC prepared by 330 nm silica spheres is located in the near-infrared region at small incident angles and will be blue-shifted to the visible region (red to green) upon increasing the incident angle. As a result, the bilayer PCs are expected to display the structural color of the bottom layer, mixing colors of each layer, and the structural color of the top layer, respectively, when the incident angle turns from 0 to 90°, realizing the color circulation of green-magenta-yellow-green.

The photographs in Figure 3a clearly illustrated that the structural color of the bilayer PCs changed from green to magenta, yellow, and then to green again upon increasing the incident angle. It can be found that the structural colors of bilayer PCs achieved a closed color loop in the CIE chromaticity diagram (Figure 3e). The SEM images in Figure

3c,d confirmed that the obtained bilayer PCs were consistent with the desired sizes.

The color variation can be explained clearly by the reflection spectra (Figure 3b). At small incident angles (0–20°), the photonic bandgap of the top PC is located at the edge of the visible region and the photonic bandgap of the bottom layer PC is located in the green region, which leads to the structural color of the bilayer PCs mainly provided by the bottom PC (green, as demonstrated in Figure 3a). With an increase in the incident angle (20–40°), the bandgap of the top layer PC is blue-shifted to the visible region (red) and the bandgap of the bottom layer PC is blue-shifted to blue-green. At this time, each layer contributes to the generation of the structural color. For example, when the incident angle is 30°, the structural color of bilayer PCs is magenta, resulting from the mixing of red and blue. Furthermore, when incident angle exceeds 45°, it can be seen from the reflection spectra that the peak generated by the bottom PC disappears. The structural color of the bilayer PCs is consistent with that of the top PCs consisting of 330 nm silica microspheres (yellow to yellow-green and to green). Thus, the structural color circulation is realized in the bilayer PC structure by changing the incident angle through bandgap engineering.

To prove the generality of this strategy, we also designed another bilayer PC structure using silica spheres with diameters of 210 and 330 nm. There is no doubt that a similar phenomenon has been observed (the specific information is shown in Figure S5). For this strategy, one key factor is the particle size of the colloidal microspheres in each layer. The acquired color can be achieved by controlling

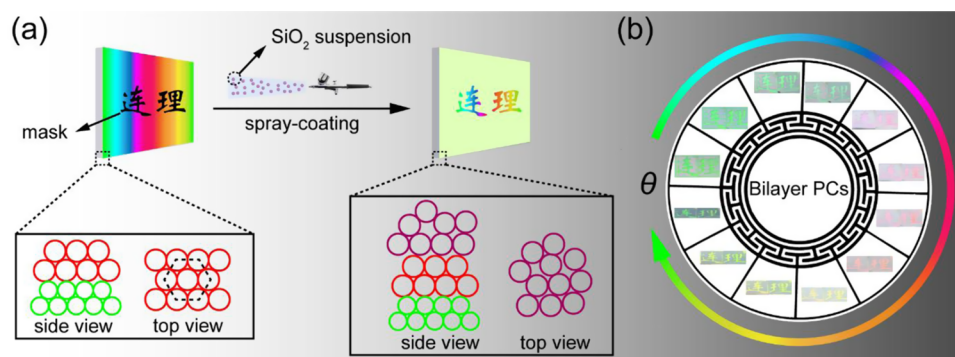


Figure 4. (a) Schematic of the patterning process using the spray-coating method. (b) Structural color of patterned bilayer PCs achieving circulation with an increase in the incident angle.

the bandgap of each layer by selecting microspheres with special size.

3.3. Patterning of the Bilayer PCs and Their Application in Anticounterfeiting. Benefiting from the easily realization of the color tuning of PCs in this bilayer structure, we extend its application to the anticounterfeiting field by patterning of the bilayer PCs with a simple spraying method. Figure 4a shows the schematic diagram of the patterning process. Specifically, a mask with a pattern of “连理” was coated on the surface of the as-prepared bilayers and the paint (suspension of silica microspheres) was sprayed with an airbrush. As illustrated in Figure 4a, the surface and cross-sectional images of the sprayed region and unsprayed region were clearly illustrated. The part covered by the mask still retained the original structure, which maintained the structural color, whereas due to the strong scattering effect, the structural color of the part without the mask covered by disordered silica microspheres disappeared (Figure S6), thereby realizing the patterning of bilayer PCs.

As shown in Figure 4b, the part covered by the mask demonstrated a vivid pattern with high angle-dependence. The structural color can vary from green to magenta, orange, yellow, and green again, which has not been achieved by single-layer PCs or other bilayer PCs. This feature allows the bilayer structure to be applied as a promising candidate for an anticounterfeiting material.

4. CONCLUSIONS

Bilayer PCs were fabricated by a simple layer-by-layer dip-coating method using silica spheres with different particle sizes. In the bilayer PC structure, the thickness of the top layer and the incident angle were crucial factors determining its optical properties. The structural colors of the bottom layer were weakened due to the enlarged scattering effects by increasing the thickness of the PC structure or the incident angle. Suitable top layer thickness permitted the bilayer structure to demonstrate the mixing structural colors of both layers at small incident angles and only the structural color of the top layer at large incident angles. As a benefit of the tunable optical properties of this bilayer, we designed a special bilayer PC structure and the structural color could achieve circulation of green to magenta, orange, yellow, and green again with the increase of the incident angle. This phenomenon is greatly different from the monodirectional blue shift of the structural color in single-layer PCs and simple supposition of the structural color in reported multilayer PCs. The enhanced tunability of the structural color in the bilayer structure

provides them strong anticounterfeiting capability and will show promising potential in this field.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b21092.

SEM images of SiO₂ microspheres used in this paper; the detailed theoretical calculations about the size of the SiO₂ based on Bragg's law; theoretical and practical values about the diameter of the SiO₂ microspheres; the schematic diagram of the measurement setup of reflectance and transmission; the schematic diagram of the method to take photos; transmission spectra of single-layer and bilayer PCs at different incident angles; digital photos and the cross-sectional SEM image of the bilayer PCs assembled from 210 and 330 nm SiO₂ nanoparticles; the surface and cross-sectional SEM images of the sprayed region of the bilayer PCs (PDF)

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Notes

The authors declare no competing financial interest.

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